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(54) METHOD OF CONDITIONING A HEAD OF HAIR

(71) We, L'OREAL, a French Body Corporate of 14, Rue Royale, 75008 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method which makes it possible to improve the condition of hair as well as the appearance of a head of hair.

It is known that, as a result of its general condition or as a result of deterioration due to the effect of atmospheric agents or to the effect of treatments such as bleaching, permanent wavings or dyeings, the hair of many people is frequently difficult to comb out and to set, especially when the head of hair is thick. The hair is generally, to varying degrees, dry, lustreless and rough or lacks "life" and "springiness".

Attempts have been made to reduce or correct these defects by applying to the hair a "hair conditioning" composition intended to improve the condition of wet and dry hair as well as to simplify combing and setting. By "hair conditioning", as used herein, is meant an operation which, whilst making it easier to untangle and comb wet hair, imparts "bulk" and elasticity to dry hair, which ensures that the set stays in well. The reagents which effect "hair conditioning" are called "conditioners".

Synthetic polymers such as polyethylene-imines, polyvinylpyridines, poly-[(p-vinyl-benzyl)-trimethyl-ammonium chloride] and poly-[diallyl-dimethyl-ammonium chloride] have already been used for conditioning hair. However, these polymers possess the disadvantage of not being compatible with anionic shampoos.

Polyamino-amide polymers, prepared by the polycondensation of a dicarboxylic acid and a polyalkylene polyamine, polyaminoureylene polymers and alkylene-polyamine polymers modified, particularly by epichlorohydrin, in roughly stoichiometric amounts relative to the amine groups of the polyamino-amide, have also already been used in compositions for treating hair. The addition of these large amount of epichlorohydrin to the polymers gives rise to the presence of reactive groups in the cross-linked polymer. These polymers in fact carry alkylating groups i.e. groups which can introduce alkyl (including substituted alkyl) substituents which can react with nucleophilic compounds such as amines, thiols and sulphites. Azetidinium rings may be mentioned as examples of such alkylating groups.

The first consequence of the existence of such reactive groups is a lack of stability of these polymers; they tend to degrade when they are left to stand in solution. Furthermore, the existence of such alkylating groups makes the application of these products to the human skin a potentially dangerous operation since they can react with it.

The use of thermosetting polymers, to be crosslinked under the action of heat, as "hair conditions" has also been proposed but their use necessarily involves a special heating step.

The aim of the present invention is to provide a "hair condition" which overcomes the disadvantages of prior art conditioners. This is achieved by using a cross-linked polyamino-polyamide which does not possess reactive groups and is, therefore, chemically stable.

According to the present invention there is provided a method of conditioning human hair which comprises applying thereto a composition (suitable for application to hair) which comprises a compatible aqueous or aqueous-alcoholic medium and at least one water-soluble crosslinked polymer which is either (I) a polymer produced by crosslinking a polyamino-polyamide (A) prepared by polycondensation of an acid compound with a polyamine; the acid compound is chosen from amongst (i) organic dicarboxylic acids, (ii) ethylenically unsaturated aliphatic mono- and di-carboxylic acids, (iii) esters of the acids defined under (i) and (ii), preferably with alkanols of 1 to 6 carbon atoms, (iv) mixtures of these compounds and (v) the product of reaction of a bis-primary amine or a bis-secondary amine with (i), (ii), (iii) or (iv), or (II) a polymer obtained by alkylating (as hereinbefore defined) a crosslinked polymer as defined above with an epoxide, ethylenically unsaturated compound, chloroacetic acid, propane-sultone or butane sultone. The polyamine is chosen from amongst bis-primary, mono- or di-secondary polyalkylene-polyamines. Up to 50 mole % for example up to 20 mol % or up to 40 mol % of this polyamine can be replaced by a bis-primary amine, preferably ethylene-diamine or hexa-methylene-diamine, or by a bis-secondary amine, preferably piperazine or a mixture of such amines.

Thus it is, for example, possible to use up to 20 mol % of hexamethylene-diamine or up to 50, for example up to 40, mol % of ethylene-diamine or piperazine per 100 mol % of total amine. Crosslinking is effected by means of a crosslinking agent (B) chosen from amongst epihalohydrins, diepoxides, dianhydrides, unsaturated anhydrides and bis-unsaturated compounds. According to the present invention, the crosslinked polymer used possesses all the following characteristics:

(1) it is prepared using 0.025 to 0.35 mol, generally 0.025 to 0.2, preferably 0.025 to 0.1 mol, of crosslinking agent per amine group of the polyamino-polyamide (A):
(2) it is preferably soluble in water to a concentration of 10% by weight, without gel formation;
(3) the apparent viscosity at a shear rate of 26.3 sec^{-1} of a 10% by weight solution of it in water at 25°C is at least 3 centipoises, usually up to 200, especially from 20 to 50, centipoises; and
(4) it does not possess any alkylating groups, and is chemically stable.

The acids used to prepare the polyamino-polyamides (A) are selected from

dicarboxylic organic acids, suitably with 6 to 10 carbon atoms, for example saturated acids such as adipic acids such as 2,2,4-and 2,4,4-trimethyl-adipic acids, and aromatic acids such as terephthalic acid, and

ethylenically unsaturated aliphatic mono- and dicarboxylic acids, for example acrylic, methacrylic and itaconic acids.

Preferred acids includes adipic acids which is particularly preferred, and the compounds resulting from the addition of an alkylene-diamine to unsaturated acids such as acrylic, methacrylic and itaconic acids and their esters. It is also possible to use the esters of the acids mentioned above. It is also possible to use mixtures of two or more carboxylic acids or their esters.

The polyamines which can be used to prepare the polyamino-polyamides (A) are bis-primary, mono- or di-secondary polyalkylene-polyamines, for example diethylene-triamine, dipropylene-triamine, triethylene-tetramine and mixtures thereof.

The polycondensation can be effected in known manner, for example, by mixing the reagents and then heating at 80° to 250°C, preferably 100° to 180°C, for 1 to 8 hours depending on the reagents used. After heating under reflux for, for example, 1/2 hour to 1 hour, the water or the alcohol formed during the polycondensation is removed, first at ordinary pressure and then under reduced pressure. The reactions suitably take place under a stream of nitrogen in order to avoid excessive colouration and to facilitate the removal of the volatile substances.

Equimolar amounts of dicarboxylic acid and amines relative to the primary amine groups of the polyalkylene-polyamines are preferably used.

According to a preferred method of preparation, the polycondensation with the polyalkylene-polyamine, preferably diethylene-triamine, triethylene-tetramine dipropylene-triamine or mixtures thereof, is carried out either (i) with a dicarboxylic acid, preferably adipic acid or its dimethyl ester, or (ii) wth the intermediate product resulting from the addition of one mol of ethylene-diamine to two mols of the methyl ester of an ethylenically unsaturated acid, such as methyl acrylate, methacrylate or itaconate.

The reactions involving the addition of ethylene-diamine to unsaturated esters can be carried out by mixing the reagents at, for example, 5° to 80°C, and the poly-

condensation reactions can be carried out by, for example, heating under reflux for 30 to 60 minutes, followed by removal of methyl alcohol at 120—150°C or water at 140—175°C, first at ordinary pressure and then under a partial vacuum of 15 mm Hg.

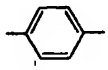
The polyamino-polyamides (A) thus obtained have a viscosity, as a 10% by weight solution in water at 25°C, of less than 3 centipoises.

The structure of the preferred polyamino-polyamides (A) can be represented by the general formula (I)

$$—[—OC—R—CO—Z—]— \qquad (I)$$

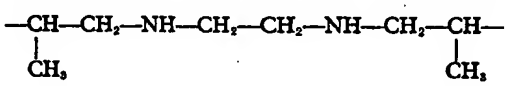
wherein R represents a divalent radical which is derived from the acid used or from the product resulting from the addition of the acid to the bis-primary or bis-secondary amine.

Preferred R radicals are:

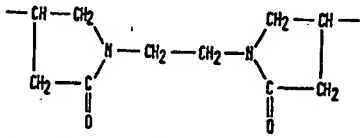


$$—(CH_2)_4—,$$

$$—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—,$$



or



These radicals are derived from, respectively, terephthalic acid, adipic acid, and the product resulting from the addition of ethylene-diamine to acrylic, methacrylic and itaconic acids or their esters.

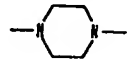
Z represents:

1) in an amount of 50 to 100 mol %, the radical

$$—NH—[—(CH_2)_x—NH—]_n— \qquad (II)$$

wherein x=2 and n=2 or 3, or alternatively,
x=3 and n=2,
this radical being derived from diethylene-triamine, triethylene-tetramine or dipropylene-triamine; and

2(a) in an amount of 0 to 50 mol %, the above radical (II), in which x=2 and n=1, and which is derived from ethylene-diamine, or the radical



derived from piperazine; or

(2)(b) in an amount of 0 to 20 mol %, the radical

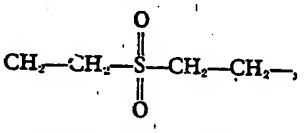
$$—NH—(CH_2)_6—NH—,$$

derived from hexamethylene-diamine.

The polyamino-polyamides thus obtained are then crosslinked by adding a crosslinking agent. The difunctional crosslinking agent may be (a) an epihalohydrin, for example epichlorohydrin; (b) a diepoxide, for example diglycidyl ether or N,N′-bis-epoxy-propyl-piperazine; (c) a dianhydride, for example butane-tetracarboxylic acid dianhydride or pyromellitic acid dianhydride; or (d) a bis-unsaturated compound, for example divinyl-sulphone or methylene-bis-acrylamide.

A preferred crosslinking agent is epichlorohydrin. Other preferred crosslinking agents are divinyl-sulphone, methylene-bis-acrylamide, diglycidyl ether and N,N′-bis-epoxy-propyl-piperazine. These crosslinking agents give rise, respectively, to the following radicals:

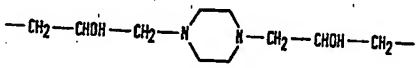
$$CH_2—CHOH—CH_2—,$$



$$—CH_2—CH_2—CONH—CH_2—NHCO—CH_2—CH_2—,$$

$$—CH_2—CHOH—CH_2—O—CH_2—CHOH—CH_2—$$

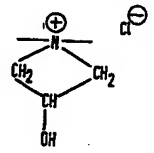
and



The crosslinking reactions are generally carried out at 20°C to 90°C, starting from a 20 to 30% by weight aqueous solution of the polyamino-polyamide, to which the cross-linking agent is added in very small portions until a large increase in viscosity is achieved, but without however reaching the stage where a gel which does not dissolve in water is produced. The concentration is then rapidly adjusted to 10% by weight by adding water, and the reaction mixture is cooled if necessary.

The proportions of crosslinking agent to be used, which vary depending on the nature of the polyamino-polyamide and of the crosslinking agent, can be determined easily by adding the desired crosslinking agent to an aqueous solution of the polyamino-polyamide until the viscosity of a 10% by weight strength solution, at 25°C, is between 3 centipoises and the gel state, whilst retaining perfect solubility in water.

Exceeding the proportions of crosslinking agent indicated above leads to the formation of a gel which cannot be diluted with water. By increasing the amount of crosslinking agent further, polymers which are soluble in water are again obtained but their character changes with time and temperature. This changing character is due to the presence in the crosslinked polymer of substituents which are reactive with respect to nucleophilic groups. When epichlorohydrin is used as the crosslinking agent, in roughly stoichiometric proportions, the reactive substituents consist mainly of azetidinium rings



The crosslinked polymers used in the compositions can be stored satisfactorily and are compatible with anionic surface-active agents whilst ensuring that wet hair can be combed out easily.

This compatibility with anionic surface-active agents can be improved further by alkylating the secondary amino groups of the cross-linked polyamino-amides. The alkylation augments the solubility of the polymer. This alkylation can be carried out using an epoxide, such as glycidol, ethylene oxide or propylene oxide, an ethylenically unsaturated compound such as acrylamide or acrylic acid, chloroacetic acid or an alkane sultone such as propane sultone or butane sultone.

By way of example, during the alkylation the primary or second amino radicals react with, for instance, acrylamide or glycidol to give, respectively, groups of the formula:

$$—\overset{|}{N}—CH_2—CH_2—CONH_2$$

and

$$—\overset{|}{N}—CH_2—CHOH—CH_2OH$$

The alkylation is suitably carried out on an aqueous solution of the cross-linked polymer, for example a 10 to 30% by weight solution, at a temperature from 10 to 95°C. The degree of alkylation relative to the total basicity of the polymer i.e. the number of mols of alkylating agent relative to the total number of amine groups, is

suitably up to 80%. The basicity index of the polymer, expressed is meq/g, gives the total number of milliequivalents of basic nitrogen atoms per gram.

The cross-linked polymers can be used in various cosmetic compositions for hair, for the treatment of normal hair and, more particularly of hair which has been rendered sensitive. They are suitably used at concentrations of 0.1 to 5%, preferably 0.2 to 2.5%, especially 0.3 to 1.3%, by weight, in, for example, shampoo compositions, colouring shampoo compositions, dyeing compositions, setting gel compositions, setting lotion compositions, "brushing" lotion compositions, rinsed lotion (rinse) compositions and non-rinsed reinforcing wavesetting lotion compositions, in compositions in combination with a hair strengthening agent, in anti-dandruff compositions and anti-seborrhoea compositions.

By "rinse", there is meant a lotion which is applied after a shampoo in order to obtain a "hair conditioning" effect and which is rinsed after waiting for a few minutes.

By "brushing lotion" or shaping lotion, there is meant a lotion which is applied after a shampoo and which promotes the shaping of the head of hair, this shaping process being carried out on wet hair, by means of a brush which is used at the same time as the hair is dried by means of a hand-held drier. This technique is suitable for relatively short hair.

By "non-rinsed reinforcing wavesetting lotion", there is meant a lotion which is applied ofter shampooing and before setting in waves, which is not rinsed out and which makes it easier to set the hair in waves and improves its shape and the way in which it holds its set.

By "strengthing lotion", there is meant a lotion which contains products which strengthen the keratinic chain of hair, for example methylol group-containing compounds, such as those described in French Patents Nos. 1,527,085 and 1,519,979. These strengthening agents are generally used in combination with cationic compounds which make it easier to comb out wet hair but possess the disadvantage of giving the hair a sticky appearance when it is dry.

The compositions used in this invention generally have a pH of 2 to 11, preferably 3 to 8. They can be in a variety of forms, such as aqueous or aqueous-alcoholic solutions, gels, creams or dispersions, or in the form of aerosols.

In addition to the cross-linked polymer, the compositions can contain any ingredient used in compositions for the hair, especially anionic, cationic, amphoteric, zwitter-ionic or non-ionic surface-active agents, synergistic agents, stabilisers, thickeners, emulsifiers, softening agents, preservatives, dyestuffs and perfumes. The compositions can also contain other cosmetic resins, in particular non-ionic, cationic or anionic resins.

Typical cosmetic resins which may be used in the compositions of the present invention include 10 molar % crotonic acid-90 molar % vinyl acetate copolymers having a molecular weight from 10,000 to 70,000, vinyl pyrrolidone-vinyl acetate copolymers having a molecular weight from 30,000 to 360,000, the molar ratio of the components being from 30 to 70 to 70 to 30, quaternary polyvinylpyrrolidones having a molecular weight of the order of 1,000,000 such as that sold under the trade name "Gafquat 755" (a Registered Trade Mark of GAF Corporation), cationic polymers resulting from the condensation of piperazine or a derivative or either (i) a difunctional compound such as an alkyl or alkylaryl dihalide, a bis-epoxide, an epihalohydrin or a bis-unsaturated compound and/or (ii) a primary amine, the two hydrogen atoms of which are optionally substituted and which carries a bifunctional compound, (iii) an epihalohydrin and a hydroxylated amine such as diglycolamine, 2-amino-2-methyl-1,3-propanediol or an epihalohydrin and an amino-acid such as glycolic acid.

Amongst the surface-active agents which may be used there may be mentioned anionic surface-active agents such as alkali metal or alkanolamine salts of sulphonated alkanes, alkyl sulphates and alkyl ether sulphates and their products of condensation with ethylene oxide, for example sodium or triethanolamine lauryl or myristyl ether sulphate, the semi-ester alkanol amine of disodiumsulphosuccinate; non-ionic surface-active agents such as the products of condensation of a monoalcohol, an α-diol or an alkyl phenol with glycidyl, for example the compounds of the formula:

$$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_n—H$$

in which R represents an aliphatic, cycloaliphatic or aryl aliphatic radical of 7 to 21 carbon atoms, the aliphatic chain optionally containing ether, thioether or hydroxymethyl radicals and n is greater than or equal to 1 and less than or equal to 10, the compounds of the formula:

$$RO—[—C_2H_3O(CH_2OH)—]_n—H$$

in which R represents an alkyl, alkenyl or alkylaryl radical and n is a number less than or equal to 10; cationic surface-active agents such as dimethylhydroxymethyl cetylammonium chloride and tetradecyltrimethylammonium bromide and amphoteric surface-active agents such as carboxylic derivatives of imidazole.

The compositions used in the present invention also preferably contain an electrolyte. The presence of electrolyte in the composition reduces or eliminates entirely the tendency for sensitive hair to accumulate the polymers. Suitable electrolytes include alkali metal and alkaline earth metal salts of mineral and organic acids which are soluble in water, preferably sodium, potassium, calcium or ammonium acetate or chloride. The quantity of electrolyte is not critical but is preferably from 0.01 to 5%, especially 0.4 to 3%, by weight based on the weight of the composition. The ratio by weight between the electrolyte and the polymer is generally from 0.1:1 to 1.5:1.

The combination of the conditioners used in the present invention with non-ionic surface-active agents provides particularly valuable shampoos because their application makes it easier to comb out hair.

In our Application No. 22556/77 (Serial No. 1494916) we described and claim a composition suitable for application to human hair comprising water or an aqueous alcohol and a polymer of the present invention and which possesses one or more of the following characteristics:

(i) it is in the form of a shampoo and contains an anionic, cationic, non-ionic or amphoteric surface-active agent;

(ii) it contains one or more additives suitable for application to hair selected from an anti-seborrhoeic agent, an anti-dandruff agent, a hair strengthening agent, a hair resin, a perfume an electrolitic hair desensitising agent and a cationic or non-ionic surface-active agent.

The following Examples further illustrate the present invention. Examples I to 10 illustrate the preparation of the polymers. All parts and percentages are by weight unless otherwise stated.

EXAMPLE I

Polycondensation of adipic acid and diethylene-triamine.

The structure of the polymer obtained can be characterised by the following unit:

$$OC—(CH_2)_4—CONH—(CH_2—CH_2—NH)_2—$$

876 g (6 mols) of adipic acid are added, with stirring and in a nitrogen atmosphere, over the coure of 15 minutes, to 619 g (6 mols) of diethylene-triamine. The reaction mixture is then heated at 145—150°C, at which temperature condensation water is noted. Refluxing is maintained for 45 minutes and then the water is removed by distillation at ordinary pressure for 2 hours and then under reduced pressure (15 mm Hg) for 1 hour. The heating temperature increases gradually to 170°C.

The product thus obtained is cast when hot. After cooling, it is in the form of a hard and brittle resin. It is a transparent yellow-green colour and dissolves completely in water.

EXAMPLE Ia

Crosslinking of the polymer prepared according to Example I, using epichlorohydrin.

9 g of epichlorohydrin are added, with stirring, to 200 g of resin, prepared according to the process described in Example I, dissolved in 800 g of water. The mixture is heated to 90°C and then 1.8 g of epichlorohydrin are added in very small portions and at intervals of 5 to 10 minutes until a viscosity greater than 50 centipoises at 65°C is obtained.

The solution is then diluted immediately until its solids content is 10%, by adding 1,098 g of water.

The apparent viscosity, measured after 24 hours and at 25°C, is 31 centipoises at a rate of shear of 26.3 seconds^{-1}.

The amount of crosslinking agent used is 11 mols of epichlorohydrin per 100 amine groups.

EXAMPLE Ib

Crosslinking of the polymer prepared according to Example I, using methylene-bis-acrylamide.

7 g of methylene-bis-acrylamide are added, at ambient temperature and with stirring, to 70 g of resin prepared according to the process described in Example I and dissolved in 280 g of water, and then the mixture is heated to 80—90°C. After heat-

ing for 1 hour, a large increase in the viscosity is observed. The mixture is then diluted until its solids content is 10%, by adding 413 g of water.

A clear solution is obtained with an apparent viscosity of 32 centipoises, measured after 24 hours, at 25°C, and under a rate of shear of 26.3 seconds^{-1}.

The amount of crosslinking agent used is 12.1 mols of methylene-bis-acrylamide per 100 amine groups of the polyamino-polyamide.

EXAMPLE Ic

Crosslinking of the polymer prepared according to Example I, using N,N' -bis-epoxy-propyl-piperazine.

1.50 g of N,N'-bis-epoxy-propyl-piperazine are added, at ordinary temperature and with stirring, to 20 g of polymer prepared according to the process described in Example I and dissolved in 80 g of water, and then the mixture is heated to 70—80°C. After heating for 15 minutes, a gel is obtained which is diluted immediately until its solids content is 10%, by adding 113.5 g of water.

A clear solution is obtained with a viscosity of 32 centipoises measured after 24 hours, at 25°C, and under a rate of shear of 26.3 seconds^{-1}. The amount of crosslinking agent used is 7.3 mols of N,N'-bis-epoxy-propyl-piperazine per 100 amine groups of the polyamino-polyamide.

EXAMPLE Id

Crosslinking of the polymer prepared according to Example I, using divinyl-sulphone.

1.7 g of divinyl-sulphone are added dropwise, at ambient temperature, to 20 g of polymer prepared according to Example I and dissolved in 80 g of water, until gelling starts. The mixture is then diluted rapidly with 100 ml of water.

The apparent viscosity of a 10% strength solution, measured after 24 hours, at 25°C and at a rate of shear of 26.3 seconds^{-1}, is 27 centipoises.

The amount of crosslinking agent used is 13.9 mols of divinyl-sulphone per 100 amine groups of the polyamino-polyamide.

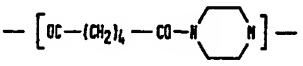
EXAMPLE II

Polycondensation of adipic acid and a mixture of diethylene-triamine and piperazine.

The structure of the polymer prepared can be represented by the two units below, in the proportions of 2:1.

$$—[OC—(CH_2)_4—CONH—(CH_2—CH_2—NH)_2]—$$

and



A mixture of 438 g (3 mols) of adipic acid and 86 g (1 mol) of piperazine is heated, with stirring, and in a nitrogen atmosphere, for 2 hours at 120—135°C. 206 g (2 mols) of diethylene-triamine are then added, at this temperature and over the course of 90 minutes. The water formed is distilled for 1 hour at 140—170°C at ordinary pressure, and then for 1 hour at 170—175°C under 15 mm Hg.

The product thus obtained is in the form of a yellow-green coloured, transparent, brittle, hard resin.

EXAMPLE IIa

Crosslinking of the polymer prepared according to Example II, using epichlorohydrin.

9 g of epichlorohydrin are added, with stirring, at ordinary temperature, to 200 g of resin, prepared according to Example II and dissolved in 800 g of water. The mixture is then heated to 90°C and a further 1.1 g of epichlorohydrin are added in small portions at 5 or 10 minute intervals, until a viscosity of 50 centipoises is reached.

The solution is then diluted rapidly with 1,091 g of water in order to obtain a concentration of 10%.

The solution thus obtained is clear and its viscosity, measured after 24 hours, at 25°C, and at a rate of shear of 26.3 seconds^{-1}, is 52 centipoises.

The amount of crosslinking agent used is 13.2 mols of epichlorohydrin per 100 amine groups of the polyamino-polyamide.

EXAMPLE III

Polycondensation of adipic acid and triethylene-tetramine.

The structure of the polymer prepared in this example can be represented by the unit:

$$—OC—(CH_2)_4—CONH—(CH_2—CH_2—NH)_3—$$

292 g (2 mols) of adipic acid are added in small portions and with stirring, under a nitrogen atmosphere, over the course of 20 minutes, to 292 g (2 mols) of triethylene-tetraamine. The mixture is then heated under full reflux at 145°C for 1 hour. The water formed is removed by distillation at ordinary pressure for 3 hours and under a reduced pressure of 15 mm of mercury for 1 hour, whilst gradually raising the temperature to 170—175°C.

A yellow-brown coloured transparent resin is thus obtained, a 10% strength solution of which possesses a viscosity, at 25°C, of less than 2 centipoises.

EXAMPLE IIIa

Crosslinking of the polymer prepared according to Example III, using epichlorohydrin.

1.8 g of epichlorohydrin are added, rapidly and with stirring, to 200 g of a 20% strength aqueous solution of polymer prepared according to the process described in Example III, and the mixture is heated at 90—95°C for 30 minutes. 0.4 g of epichlorohydrin is then added, at the same temperature, very slowly until a viscosity of more than 50 centipoises, measured at 65°C, is reached.

The solution is then diluted immediately until its solids content is 10%, by adding 220 g of water. The solution obtained is clear. Its viscosity at 25°C and at a rate of shear of 26.3 seconds^{-1} is 24 centipoises. The total amount of epichlorohydrin added is 0.0242 mol, which corresponds to 7.8 mols of crosslinking agent per 100 amine groups of the polyamino-polyamide.

EXAMPLE IIIb

Crosslinking of the polymer prepared according to Example III, using methylene-bis-acrylamide.

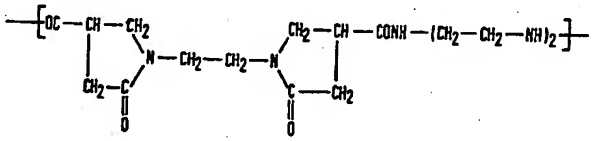
0.8 g of methylene-bis-acrylamide is added to 100 g of a 20% strength aqueous solution of polymer prepared according to the process described in Example III, and then the mixture is heated at 70—80°C for 25 minutes. A soft gel is then obtained which is diluted immediately until its solids content is 10%, by adding 108 g of water. The solution obtained is clear. Its viscosity, measured after 24 hours, at 25°C and at a rate of shear of 26.3 seconds^{-1}, is 43 centipoises.

The amount of methylene-bis-acrylamide added is equivalent to 3.4 mols of crosslinking agent per 100 amine groups of the polyamino-polyamide.

EXAMPLE IV

Polycondensation of the product resulting from the reaction of 2 mols of methyl itaconate and 1 mol of ethylene-diamine with diethylene-triamine.

The structure of the polymer prepared in this example can be represented by the unit:



First Step

118 g (1.95 mols) of ethylene-diamine are added, oxer the course of one hour, with stirring and under a nitrogen atmosphere, to 620 g (3.9 mols) of methyl itaconate, whilst keeping the temperature at 30°C.

After the mixture has been left overnight at ambient temperature, it is heated to 80°C in order to remove the methanol, first at ordinary pressure and then under a reduced pressure of 15 mm Hg. The appearance of a precipitate is then noted. The reaction mixture is taken up in 500 ml of benzene and the methanol-benzene azeotrope is distilled.

The mixture is concentrated and the residue is taken up in acetone. N,N'-Ethylene-bis-2-[4'-methylcarboxylate-pyrrolidone], in the form of a white powder with a melting point of 141—142°C and a saponification index of 6.35 milliequivalents/gram, is thus obtained in an 82% yield.

Second step

65.5 g (0.63 mol) of diethylene-triamine are added, at ambient temperature, to 198 g (0.63 mol) of the diester thus prepared, and the methanol formed is distilled by heating at 120—130°C, first at ordinary pressure for 90 minutes and then under a reduced pressure of 15 mm Hg for 30 minutes.

A yellow-green coloured, brittle, hard, transparent resin, which is perfectly soluble in water, is thus obtained.

EXAMPLE IVa

Crosslinking of the polymer prepared according to Example IV, using epichlorohydrin.

13 g of epichlorohydrin are added, with stirring, at ambient temperature, to 200 g of resin dissolved in 800 g of water. The mixture is heated to 90°C and a further 2 g of epichlorohydrin are added, in small portions, at 5 or 10 minute intervals, until gelling starts. The mixture is then diluted rapidly with 1,135 g of cold water in order to bring the solids content of the solution to 10%.

A clear solution is thus obtained, the viscosity of which, measured after 24 hours, at 25°C and at a rate of shear of 26.3 seconds $^{-1}$, is 49 centipoises.

The amount of epichlorohydrin used corresponds to 22 mols per 100 amine groups of the polyamino-polyamide.

EXAMPLE IVb

Crosslinking of the polymer prepared according to Example IV, using methylene-bis-acrylamide.

1.5 g of methylene-bis-acrylamide are added, at ambient temperature and with stirring, to 50 g of polymer prepared in Example IV and dissolved in 200 g of water, and then the mixture is heated to 85—90°C. The crosslinking agent is then added gradually until a viscosity of more than 50 centipoises at 65°C is reached. The concentration of the mixture is then brought back to a 10% solids content, by adding 285 g of water.

A clear solution with a viscosity of 54 centipoises at 25°C and at a shear rate of 26.3 seconds $^{-1}$ is obtained.

The amount of methylene-bis-acrylamide added is 3.9 g and corresponds to 16 mols per 100 amine groups of the polyamino-polyamide.

EXAMPLE V

Polycondensation of a reaction product of 2 mols of methyl acrylate and 1 mol of ethylene-diamine with diethylene-triamine.

The structure of the polymer prepared in this example can be represented by the unit:

$$—OC—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2— CONH—(CH_2—CH_2—NH—)_2—$$

689 g (8 mols) of methyl acrylate are added, over the course of 2 hours, at a temperature of between 10° and 20°C, with stirring and under a nitrogen atmosphere, to 240 g (4 mols) of ethylene-diamine. After stirring for 1 hour at ambient temperature, 413 g (4 mols) of diethylene-triamine are added. The methanol formed is then distilled by heating at 120—140°C for 2 hours at ordinary pressure and for 2 hours under a reduced pressure of 15 mm Hg.

A yellow-orange coloured transparent resin is thus obtained which, in the form of a solution with a 10% solids content, has a viscosity of less than 2 centipoises at 25°C.

EXAMPLE Va

Crosslinking of the polymer prepared according to Example V, using epichlorohydrin.

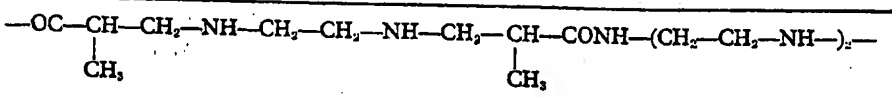
45 g of epichlorohydrin are added, with stirring, at ambient temperature, to 200 g of polymer, prepared according to the process of Example V, dissolved in 800 g of water. The mixture is heated gradually to 90°C and then 11 g of epichlorohydrin are added, in small portions, at 5 or 10 minute intervals, until gelling starts. The concentration is then diluted rapidly to a 10% solids content, by adding 1,504 g of cold water.

A clear solution is thus obtained with a viscosity of 25 centipoises, measured after 24 hours, at 25°C and at a rate of shear of 26.3 seconds $^{-1}$.

EXAMPLE VI

Polycondensation of a reaction product of 2 mols of methyl methylacrylate and 1 mol of ethylene-diamine with diethylene-triamine.

The structure of the polymer prepared in this example can be represented by the unit:



600 g of methyl methacrylate (6 mols) are added, at ambient temperature, to 180 g (3 mols) of ethylene-diamine. The mixture is left to stand for 3 days and is then heated to 80°C for 3 hours. 309 g of diethylene-triamine (3 mols) are then added and the whole is heated at 120—125°C for 4 hours at ordinary pressure and for 90 minutes under a pressure reduced to 15 mm Hg. The polycondensate thus obtained is in the form of a green-bronze coloured resin.

EXAMPLE VIa

Crosslinking of the polymer prepared according to Example VI, using methylene-bis-acrylamide.

27.3 g of methylene-bis-acrylamide are added, at ambient temperature and with stirring, to 84.6 g of polymer prepared according to the process described in Example VI and dissolved in 338.4 g of water. The mixture is then heated at 85—90°C for 15 minutes. A gel is then obtained which is diluted immediately until it has a solids content of 10%, by adding 669 g of water. A clear solution with a viscosity of 53 centipoises at 25°C and a rate of shear of 26.3 seconds^{-1} is obtained.

The amount of crosslinking agent added corresponds to 21.4 mols per 100 amine groups of the polyamino-polyamide.

EXAMPLE VII

Alkylation with propanesultone of the cross-linked polymer of Example I(a).

To 3,000 g of a 10% aqueous solution of the crosslinked polyamino-amide prepared according to Example I(a) (basidity index 0.45 meq/g; 1 g of polymer contains 0.45×10^{-3} amine groups) are added with stirring under a nitrogen atmosphere 11.35 g (0.93 mol) of propanesultone. The reaction mixture is then heated to 60°C. for 4 hours. It is diluted with 1020 g of water to reduce the concentration to 10%. The solution thus obtained has a yellow colour and possesses a viscosity at 25°C. of 12.6 cps.

EXAMPLE VIII

Alkylation with sodium chloroacetate of the cross-linked polymer of Example I(a).

To 2,000 g of solution obtained according to Example I(a) are added with agitation at ambient temperature 70 g (0.6 mol) of sodium chloroacetate and the reaction mixture is then heated at 90°C. for 10 hours. To 70 g of water are then added to reduce the concentration to 10%. A clear solution is thus obtained having a pale yellow colour and a viscosity at 25°C. of 21 cps.

EXAMPLE IX

Alkylation with glycidol of the cross-linked polymer of Example I(a).

To 1,000 g of a 10% solution of the cationic polymer are added over 2 hours with stirring at ambient temperature 27 g (0.36 mol) of glycidol. Stirring is maintained for five hours and then the resulting mixture is diluted with 265 g of water to give a 10% solution. A clear solution is thus obtained, slightly coloured, having a viscosity, measured at 25°C., of 13.8 cps.

EXAMPLE X

Alkylation with acrylamide of the cross-linked polymer of Example I(a).

To 1,000 g of a 10% aqueous solution of the polyaminoamide of Example I(a) are added at ambient temperature in the presence of a trace of sodium nitrite 20 g (0.28 mol) of acrylamide. The reaction mixture is then heated for 10 hours at 60°C. After adding 180 g of water a clear solution of polymer (10%) is obtained having a viscosity at 25°C. of 11.2 cps.

EXAMPLE A1

Anionic shampoo

Triethanolamine lauryl sulphate	15 g
Copra diethanolamide	3 g
Polymer prepared according to Example Ia	1.5 g
Water, q.s.p.	100 g
pH=7	

Approximately 10 cm^3 of this solution are applied to a head of hair which has been moistened beforehand. The head of hair is massaged lightly. The hair is rinsed

with water and a second application is effected. The head of hair is massaged vigorously in order to produce a large amount of foam, a minute is allowed to pass in order to ensure that the polymer is fixed to the hair, and then the head of hair is rinsed.

It is found that the wet hair can be combed out very easily (the comb slips readily through the hair), the hair is very soft, supple and easy to handle, and can be set in waves very easily. After drying and when the dry hair is being set, it is also found that the head of hair can be combed out easily. The hair is full of life and easy to manage.

EXAMPLE A2

Anionic shampoo	
Modified alkanolamide disodium sulphosuccinate semi-ester (sold commercially under the tradename "Monomate DHL 50"	15 g
Sodium lauryl-ether-sulphate, condensed with 2.2 mols of ethylene oxide	15 g
Polymer prepared according to Example Ia	1 g
Water, q.s.p.	100 g
pH=7.8	

EXAMPLE A3

Anionic shampoo	
Sodium lauryl-ether-sulphate condensed with 2.2 mols of ethylene oxide	12 g
Copra diethanolamide	4 g
Polymer according to Example Va	1.5 g
Quaternary polyvinylpyrrolidone copolymers with a molecular weight of the order of 1,000,000, sold commercially under the Registered Trade Mark "Gafquat 755" by GAF Corp.	0.3 g
Water, q.s.p.	100 g
pH=7.5	

EXAMPLE A4

Anionic shampoo	
Sodium myristyl-ether-sulphate, condensed with 2.5 mols of ethylene oxide	5 g
Sodium lauryl-ether-sulphate, condensed with 2.2 mols of ethylene oxide	1 g
Polymer according to Example IVa	1 g
Water, q.s.p.	100 g
pH=8	

EXAMPLE A5

Anionic shampoo	
Triethanolamine lauryl sulphate	10 g
Monoethanolamide of copra fatty acids	1.5 g
Hydrolysate of proteins derived from collagen containing 80% of active materials, sold commercially under the Registered Trade Mark "Hydropro 220" by "Stepan" Chemicals	5 g
Polymer according to Example IIa	2 g
Water, q.s.p.	100 g
pH=4	

The effect of the shampoos A2 to A4 is similar to that of the shampoo A1. The shampoo A5 also improves the condition of damaged hair by making the fibres stronger and the hair harder.

EXAMPLE A6

Non-ionic shampoo	
$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_{3.5}—H$	14 g
R=mixture of decyl and dodecyl radicals	
Polymer according to Example Ia	2.5 g
Lactic acid, q.s.p. pH=5	
Water, q.s.p.	100 g

EXAMPLE A7

Non-ionic shampoo

$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_{3.5}—H$	12 g
Dimethyl-hydroxymethyl-cetyl ammonium chloride	1.5 g
Polymer prepared according to Example Ia	1.5 g
Quaternary polyvinylpyrrolidone copolymers with a molecular weight of the order of 1,000,000 sold commercially under the Registered Trade Mark "Gafquat 755" by General Aniline and Film Corp.	0.2 g
Lactic acid, q.s.p. pH 3	
Water, q.s.p.	100 g

EXAMPLE A8

Non-ionic shampoo

$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_{3.5}—H$	5 g
R=mixture of nonyl to dodecyl	
Dimethyl-hydroxyethyl-cetyl-ammonium chloride	1 g
$C_{12}H_{25}O—[CH_2—\underset{\displaystyle CH_2OH}{\underset{|}{CH}}—O—]_4—H$	5 g
Polymer of Example Va	3 g
Lactic acid, q.s.p. pH 5	
Water, q.s.p.	100 g

EXAMPLE A9

Non-ionic shampoo

Oxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	7 g
Lauryl diethanolamide	3 g
Polymer according to Example Ia	0.5 g
Polymer according to Example IIa	0.8 g
Lactic acid, q.s.p. pH 4.5	
Water, q.s.p.	100 g

EXAMPLE A10

Non-ionic shampoo

Oxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	6 g
$C_{12}H_{25}O—[CH_2—\underset{\displaystyle CH_2OH}{\underset{|}{CH}}—O—]_4—H$	4 g
Lauryl diethanolamide	1.5 g
Polymer according to Example IVa	2 g
Lactic acid, q.s.p. pH 3	
Water, q.s.p.	100 g

The non-ionic shampoos of Examples A6—A10 can be applied in the same way as the anionic shampoos of Examples A1—A5. It is found that wet hair and dry hair can be combed out very easily, with excellent results, and the hair retains suppleness and great lightness. The head of hair has bulk and can be set in waves easily.

EXAMPLE A11

Wavesetting reinforcer.

The following lotion is prepared:

90/10 vinyl acetate/crotonic acid copolymer, MW=10,000	2.5 g
Polymer according to Example Ia	0.3 g
2-Amino-2-methyl-propane-1,3-diol, q.s.p. pH 7	
Ethanol, q.s.p. 50° strength	
Dyestuff	0.01 g
Perfume	0.2 g
Water, q.s.p.	100 ml

EXAMPLE A12

Wavesetting reinforcer for greasy hair

The following lotion is prepared:

Polymer according to Example Ia	0.3 g
90/10 vinyl acetate/crotonic acid copolymer MW=50,000	2.5 g
60/40 vinylpyrrolidone)/vinyl acetate copolymer (viscosity 3.3 centipoises as a 5% solution in ethanol at 25°C.)	0.5 g
2-Amino-2-methyl-propane-diol, q.s.p. pH 7	
Ethanol, q.s.p. 50° strength	
Dyestuff	0.01 g
Perfume	0.2 g
S-Carboxymethylcysteine (to counteract seborrhoea)	0.7 g
Water, q.s.p.	100 ml

The lotions of Examples A11 and A12 can be applied to wet hair which is towelled dry, after shampooing and before being wound up in order to set it in waves.

It is found that wet hair can be combed out easily. After the hair has been wound up in order to set it in waves, it is found that the hair has more life, is softer and is slightly more glossy. The set stays in for a considerably longer period.

EXAMPLE A13

Lotion for "brushing" (shaping)

The following lotion is prepared:

Polymer according to Example Ia	0.5 g
Ethanol, q.s.p. 50° strength	
Dyestuff	0.01 g
Perfume	0.2 g
Water, q.s.p.	100 ml

This lotion is applied to wet hair which has been towelled dry after shampooing. The head of hair is shaped by means of a brush whilst drying the hair by means of a hand-held drier.

It is found that the brush passes (through the hair) very easily and that the set stays in for a long time. It is also found that the hair is glossier and softer.

EXAMPLE A14

Rinse (rinsed lotion) for fine soft hair.

The following lotion is prepared:

30/70% cetyl/stearyl alcohol, oxyethyleneated to the extent of 33%, sold commercially under the Registered Trade Mark "Sipol Wax AO" by "Sinnova"	1.5 g
Dimethyl-distearyl-ammonium chloride, sold commercially under the Registered Trade Mark "Arquad 2HT 75" by "Armour"	1.5 g
$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_{3.5}—H$ R=mixture of noyl to dodecyl	1 g
Polymer according to Example IIa	2 g
Quaternary polyvinylpyrrolidone copolymers with a molecular weight of the order of 1,000,000 sold commercially under the Registered Trade Mark "Gafquat 755" by General Aniline & Film Corp.	0.5 g
Hydroxyethyl-cellulose	0.9 g
Maleic acid, q.s.p. pH 8	
Water, q.s.p.	100 g

This lotion is applied to wet hair which has been towelled dry after shampooing, the lotion is left in place for 5 minutes, and then the hair is rinsed.

It is found that wet hair can be combed out very easily. After the hair has been set in waves and dried, it is full of life, easy to manage and glossy.

EXAMPLE A15

Setting lotion.

The following lotion is prepared:

Polymer according to Example Va	0.5 g
Silicone oil	0.1 g
Hydroxyethyl-cellulose	0.2 g
Ethanol	50 ml
Perfume	0.2 g
Water, q.s.p.	100 ml

This lotion, for men, is applied to wet hair. The hair is set and then dried. It is found that the hair is full of life and slightly harder and stays in place perfectly.

EXAMPLE A16

Setting gel.

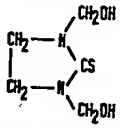
Polymer according to Example Ia	1 g
Hydroxyethyl-cellulose	2 g
Silicone Oil	0.5 g
Ethanol	40 ml
Perfume	0.02 g
Water, q.s.p.	100 g

When a small amount of this gel is applied to dry hair, it ensures that the set stays in well, whilst making the hair glossy.

EXAMPLE A17

Structuring lotion, with no rinsing.

Dimethylol-ethylene-thiourea of the formula



0.5 g

Polymer according to Example Ia	0.5 g
Phosphoric acid, q.s.p. pH 3	
Water, q.s.p.	100 ml

This lotion is applied to hair which has been washed and towelled dry after shampooing, and before setting it in waves. It is found that, when wet, the hair can be combed out easily and that it feels silky.

After being set in waves and dried, the hair is glossy and full of life; it possesses body and bulk and is soft to the touch.

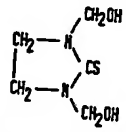
EXAMPLE A18

A similar result is obtained by replacing the polymer prepared according to Example Ia by the polymer prepared according to Example IIa.

EXAMPLE A19

Structuring lotion, applied with rinsing.

Dimethylol-ethylene-thiourea, of the formula



1 g

Polymer according to Example Ia	1 g
Phosphoric acid, q.s.p. pH 3	
Water, q.s.p.	100 ml

This lotion is applied to clean wet hair. It is left in position for 10 minutes and then the hair is rinsed.

The hair feels soft and can be combed out easily.

After the hair has been set in waves and dried, the comb passes easily through the hair which is glossy, full of life and bulky.

EXAMPLE A20

An equally good result is obtained when, in the above lotion, the polymer according to Example Ia is replaced by the polymer according to Example IIa.

EXAMPLES A21—A22

Wavesetting lotion for hair which has been rendered sensitive.

A21. An aqueous solution of the compound prepared in Example Id, containing 1% of active material and 0.5% NaCl and adjusted to pH 7 by means of citric acid, is prepared.

It is applied to bleached hair. The hair is set in waves and dried.

The hair is hardened and full of life; it feels silky and is easy to comb out.

A22. An aqueous solution of the compound prepared in Example Ic, containing 1% of active material and 1.5% NH_4Cl and adjusted to pH 5 by means of lactic acid, is prepared. It is applied to bleached hair. The hair is set in waves and dried. The hair is hardened. It is elastic and glossy. It feels silky and is easy to comb out.

EXAMPLE A23

Treatment lotion, applied with rinsing.

25 ml of the following solution are applied to clean wet hair:

Polymer according to Example Ib	1.5 g
Citric acid, q.s.p. pH 5	
Water, q.s.p.	100 g

The solution is left in position for 5 minutes and the hair is rinsed. The hair feels soft and can be combed out easily. The hair is now set in waves and dried. The dry hair can be combed out easily. It is glossy and full of life.

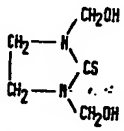
EXAMPLE A24

The same result is obtained by replacing 1.5 g of polymer according to Example Ib by 1 g of polymer according to Example IIIa.

EXAMPLE A25

Structuring lotion, applied without rinsing.

Dimethylol-ethylene-thiourea, of the formula



0.6 g

Polymer according to Example IIIb	0.5 g
Phosphoric acid, q.s.p. pH 3	
Water, q.s.p.	100 g

The mixture is applied to hair which has been washed and towelled dry, before setting it in waves. The hair can be combed out easily and feels silky. It is now set in waves and dried.

The hair is glossy, full of life, elastic and bulky. It feels silky and is easy to comb out.

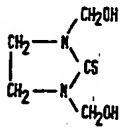
EXAMPLE A26

The same result is obtained if the polymer according to Example IIIb is replaced by the polymer according to Example IVb.

EXAMPLE A27

Structuring lotion, applied without rinsing.

Dimethylol-ethylene-thiourea, of the formula



1.5 g

Polymer according to Example VIa	1 g
Hydrochloric acid, q.s.p. pH 3	
Water, q.s.p.	100 g

The mixture is applied to hair which has been washed and towelled dry. It is left in position for 10 minutes and the hair is rinsed. The hair is easy to comb out and feels soft and silky. It is set in waves and dried under a hood.

The dry hair can be combed out easily; it is glossy, full of life and bulky.

EXAMPLE A28

Anionic shampoo.

Anionic shampoo.	
Monoethanolamide lauryl sulphate	10 g
Monoethanolamides of copra fatty acids	1.5 g
Polymer according to Example Ic	1 g
Lactic acid, q.s.p, pH 7.2	
Water, q.s.p.	100 g

EXAMPLE A29

Anionic shampoo.

Oxyethyleneated sodium lauryl-ether-sulphate containing 2.2 mols of ethylene oxide	6 g
Triethanolamine lauryl sulphate	6 g
Diethanolamides of copra fatty acids	3 g
Polymer according to Example IIIa	1.5 g
Lactic acid, q.s.p. pH 7.6	
Water, q.s.p.	100 g

EXAMPLE A30

Anionic shampoo.

Same composition as the shampoo of Example A29, except that the polymer according to Example IIIa is replaced by the polymer according to Example IIIb.

EXAMPLE A31

Anionic shampoo.

Oxyethyleneated sodium myristyl-ether-sulphate, containing 2.5 mols of ethylene oxide	6 g
Oxyethyleneated monoethanolamine lauryl-ether-sulphate, containing 2 mols of ethylene oxide	9 g
Diethanolamide of copra fatty acids	3.5 g
Hydrolysate of proteins derived from collagen, containing 80% of active materials, sold under the Registered Trade Mark of "Hydropro 220" by Stepan Chemicals	3 g
Polymer according to Example IVb	1 g
Lactic acid, q.s.p. pH 7.5	
Water, q.s.p.	100 g

EXAMPLE A32

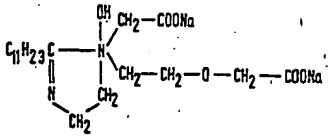
Anionic shampoo.

Same composition as the shampoo of Example A31 except that the polymer according to Example IVb is replaced by the polymer according to Example VIa.

The effect of the shampoos of Examples A28 to A30 is similar to that of the shampoo of Example A1. The shampoos of Examples A31 and A32 also improves the condition of damaged hair, making the fibres stronger and the hair harder.

EXAMPLE A33

Non-ionic shampoo.

$C_{12}H_{23}O—[—C_2H_3O(CH_2OH)—]_n—H$ *n* represents an average statistical value of approximately 4	6 g
Oxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	6 g
Carboxylic acid derivative of the imidazole of the formula 	4 g
Polymer according to Example IIIb	1 g
Lactic acid, q.s.p. pH 5	
Water, q.s.p.	100 g

EXAMPLE A34

Same composition as the shampoo of Example A33, except that the polymer IIIb is replaced by the polymer Ic.

EXAMPLE A35

Same composition as the shampoo A33, except that the polymer IIIb is replaced by the polymer IIIa.

EXAMPLE A36

Non-ionic shampoo.

Oxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	10 g
Monoethanolamides of copra fatty acids	1.5 g
Lauryl-di-methyl-amine-oxide	3 g
Polymer according to Example VIa	0.5 g
Lactic acid, q.s.p. pH 3.3	
Water, q.s.p.	100 g

EXAMPLE A37

Same composition as the shampoo A36, except that the polymer according to Example VIa is replaced by the polymer according to Example IVb.

EXAMPLE A38

$C_{12}H_{25}O—[—C_2H_3O(CH_2OH)—]_n—H$ *n* represents an average statistical value of approximately 4.	5 g
$R—CHOH—CH_2—O—[—CH_2—CHOH—CH_2—O—]_n—H$ R=mixture of C_9—C_{11} alkyl radicals and *n* represents an average statistical value of approximately 3.5.	10 g
Polymer according to Example IIIb	1.5 g
Lactic acid, q.s.p. pH 5	
Water, q.s.p.	100 g

EXAMPLE A39

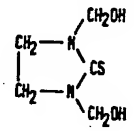
Same composition as the shampoo of Example A38, except that the polymer according to Example IIIb is replaced by the polymer according to Example IVb.

The effect of the shampoos according to Examples A33—A39 is similar to that of the shampoos according to Examples A6—A10.

Example A40

Structuring lotion, applied without rinsing.

Dimethylolethylene thiourea of formula:



0.5 g

Polymer of Example VII	0.6 g
Phosphoric acid q.s.p.	pH 3
Water q.s.p.	100 cm³

This lotion is applied to washed and dried hair after shampooing and before setting. While wet, the hair is easy to comb out and feels silky.

After setting and drying, the hair is shiny and full of life and soft to the touch.

Example A41

Lotion for increasing the volume of sensitive hair applied with rinsing.

Sodium acetate	2 g
Polymer of Example IX	2 g
Phosphoric acid q.s.p.	pH 8
Water q.s.p.	100 cm³

This lotion is applied to wet hair. The hair is soft to the touch and combs out easily.

After setting and drying, a comb passes easily through the hair which is shiny, full of life and has bulk.

Example A42

Structuring lotion applied with rinsing.

Dimethylolethylene thiourea	1 g
Polymer of Example VII	0.5 g
Polymer of Example VIII	0.4 g
Phosphoric acid q.s.p.	pH 3
Water q.s.p.	100 cm³

This lotion is applied to wet hair. It is left for 10 minutes on the hair and then rinsed.

The hair is then found to be soft to the touch and combs out easily.

After setting and drying a comb passes easily through the hair which is shiny, full of life and has bulk.

Example A43

Non-ionic shampoo.

$R—CHOH—CH_2—O—[CH_2—CHOH—CH_2—O]_{3.5}H$ $R = C_9—C_{12}$ alkyl	15 g
Polymer of Example Ia	1.5 g
NaCl	1 g
Lactic acid q.s.p.	pH 3
Water q.s.p.	100 ml.

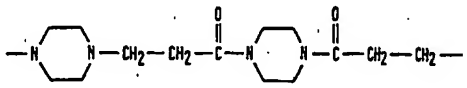
On being applied to sensitive hair this shampoo, which is clear, produces an abundant soft foam. It improves very noticeably the combing out of wet hair. After drying, the hair is full of life, light and shiny.

Example A44

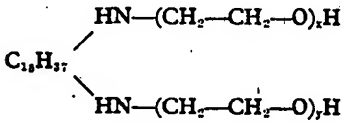
Non-ionic shampoo for sensitive hair.

$R—CHOH—CH_2—O—[CH_2—CHOH—CH_2—O]_{3.5}H$ $R = C_9—C_{12}$ alkyl	17 g
Polymer of Example Ia	0.8 g

Polymer having the recurring units:



prepared by the condensation of piperazine and piperazine bis-acrylamide (as described in British Application No. 54983/72; Serial No. 1416454) 3 g



x+y=5	1.5 g
NH_4Cl	1.2 g
Lactic acid q.s.p.	pH 3.5
Water q.s.p.	100 ml

On being applied to sensitive hair, this shampoo, which has a clear appearance, gives an abundant foam which is soft and which can readily be removed on rinsing.

The hair can be combed out without difficulty and after drying it possesses body and vitality while at the same time remaining soft and easy to manipulate.

Example A45

Non-ionic shampoo for sensitive hair.

$C_{12}H_{25}O-[C_2H_3O(CH_2OH)]_4H$	17 g
Polymer of Example IVa	1.8 g
Lauryl diethanolamide	3 g
NaCl	0.8 g
Lactic acid q.s.p.	pH 5
Water q.s.p.	100 ml

On being applied to sensitive hair, this shampoo, which has a clear appearance, gives an abundant and agreeable foam which enables one to improve the combing out of the wet hair. After drying the hair is soft, shiny and full of life while remaining manageable.

Example A46

Wave-setting reinforcer for greasy hair.

90/10 Vinylacetate/crotonic acid copolymer of molecular weight 25,000	2.5 g
60/40 vinylpyrrolidone/vinylacetate copolymer (viscosity 3.3 centipoises as a 5% solution in ethanol at 25°C.)	0.5 g
Polymer of Example VII	0.3 g
S-carboxymethylcysteine (anti-seborrheic agent)	0.7 g
Triethanolamine q.s.p.	pH 8.6
Ethylalcohol	10 ml
Water q.s.p.	100 ml

This lotion is applied to moistened and dried hair after shampooing and before rolling on setting rollers.

It was found that the wet hair was easy to comb out.

After rolling on setting rollers the hair was found to be more vital, softer and slightly more glossy. The hold of the set was considerably improved.

Example A47

Wave-setting reinforcer for greasy hair.

90/10 vinylacetate/crotonic acid copolymer of molecular weight 70,000	2.5 g
60/40 vinylpyrrolidone/vinylacetate copolymer (viscosity 4 cps as a 5% solution in ethanol at 25°C).	
Polymer of Example VII	0.5 g
Triethanolamine q.s.p.	0.3 g
Ethyl alcohol	pH 7
Water q.s.p.	10 ml
	100 ml

This solution is applied to hair which has been wetted and dried after shampooing and before winding on setting rollers.

It was found that the wet hair combed out more easily. After winding on setting rollers the hair was found to be more full of life, softer and slightly more glossy. The hold of the set was considerably improved.

Example A48

Wave-setting reinforcer for greasy hair.

90/10 vinylacetate/crotonic acid copolymer of molecular weight 50,000	2.5 g
60/40 vinylpyrrolidone/vinylacetate copolymer (viscosity 3.5 cps as a 5% solution in ethanol at 25°C)	
Polymer of Example IX	0.5 g
Triethanolamine q.s.p.	0.3 g
Ethyl alcohol	pH 7
Water q.s.p.	10 ml
	100 ml

This solution is applied to hair which has been wetted and dried after shampooing and before winding on setting rollers.

It was found that the wet hair combed out more easily. After winding on setting rollers the hair was found to be more full of life, softer and slightly more glossy. The hold of the set was considerably improved.

Example A49

Wave-setting reinforcer for dyed greasy hair.

90/10 vinyl acetate/crotonic acid copolymer of molecular weight 50,000, neutralised with triethanolamine	2.5 g
60/40 vinylpyrrolidone/vinyl acetate copolymer (viscosity 3.7 cps as a 5% solution in ethanol at 25°C)	
Polymer of Example Ia	0.5 g
Dimethyl hydroxymethyl cetylammonium chloride	0.5 g
NaCl	0.1 g
Hydrochloric acid q.s.p.	0.5 g
Ethyl alcohol	pH 8
Water q.s.p.	50 ml
	100 ml

This lotion is applied to hair which has been wetted and dried after shampooing. The coiffure is produced using a brush while drying the hair with the aid of a hand dryer.

It was found that the brush passed through the hair very well and the hold of the coiffure was better. Also, the hair is more glossy and softer.

Example A50

Structuring lotion without rinsing.

Dimethylolethylene thiourea	0.5 g
Polymer of Example 10	0.6 g
Phosphoric acid q.s.p.	pH 3
Water q.s.p.	100 ml

This lotion is applied to hair which has been washed and dried after shampooing and before setting. It was found the wet hair combed out easily and was soft to the touch.

After setting and drying, the hair is shiny and full of life. It possesses body and is soft to the touch.

Example A51

Rinsing lotion for fine, soft hair.

"Vaseline" (Registered Trade Mark) oil	7.5 g
Dimethyl distearyl ammonium chloride	1 g
$R—O—[C_2H_3O(CH_2OH)]_6H$ ($R=C_{10}—C_{14}$ alkyl)	3.75 g
$C_{12}H_{25}O—[C_2H_3O(CH_2OH)]_4H$	3.75 g
Polymer of Example IX	2 g
Quaternary copolymer of polyvinylpyrrolidone having a molecular weight of the order of 1,000,000 sold under the trade name "Gafquat 755"	2.5 g
Citric acid q.s.p.	pH 3
Water q.s.p.	100 g

This solution is applied to hair which has been wetted and dried after shampooing; after allowing it to act on the hair for 5 minutes the hair is rinsed. The wet hair was found to comb out very well.

After setting and drying, the hair is full of life, easy to handle and shiny.

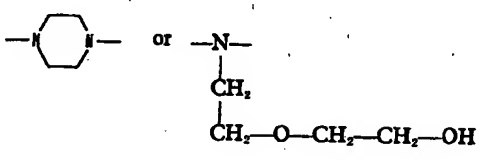
Example A52

Anionic shampoo.

Triethanolamine lauryl sulphate (40% active material)	30 g
Diethanolamine of the fatty acids of copra	1.5 g
Polymer of Example Ia (100% active material)	1 g

Polymer having the recurring units:

$—[Y—CH_2—CHOH—CH_2—]$ where Y represents



0.5 g

the two groups being present statistically

Distilled water q.s.p.	100 g

About 10 cm³ of this clear solution is applied to the head of hair previously moistened. It is massaged gently and then rinsed with water for a further application. This time it is massaged vigorously to obtain an abundant foam. The foam is allowed to remain for 1 minute to assure the fixing of the polymer to the hair and is then rinsed.

It is found that it is very easy to comb out the wet hair, the hair is very soft, supple and malleable and setting can be carried out very easily. After drying, the hair is equally easy to comb out. The hair is full of life but easy to manage.

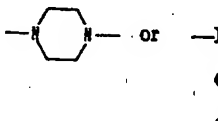
Example A53

Cationic shampoo

Tetradecyltrimethylammonium bromide	75 g
Lauryl alcohol oxyethylenated with 12 mols of ethylene oxide per mol of alcohol	50 g
Polymer of Example Ia	5 g

Polymer possessing recurring units:

$$-[Y-CH_2-CHOH-CH_2-]$$ where Y represents



Lactic acid q.s.p.	5 g
Distilled water q.s.p.	pH 5—5.5
	1000 g

This solution, which is clear, is applied to dyed hair. After massaging it in, the hair is rinsed with water and then a second quantity of shampoo is applied. The head of hair is massaged vigorously to obtain an abundant foam and this is then rinsed off.

It is found that the wet hair is very easy to comb out, the hair is very soft, supple and malleable and setting can be carried out very easily. After drying and during the drying likewise it is easy to comb out the hair. The hair is full of life and easy to manage.

WHAT WE CLAIM IS:—

1. A method of conditioning human hair which comprises applying thereto a composition comprising a compatible aqueous or aqueous alcoholic medium and at least one water-soluble crosslinked polymer which is either (I) a polymer produced by crosslinking a polyamino-polyamide prepared by polycondensation of an acid compound which is either: (i) an organic dicarboxylic acid, (ii) an ethylenically unsaturated aliphatic mono- or dicarboxylic acid, (iii) an ester of an acid as defined under (i) or (ii), (iv) a mixture of two or more compounds as defined under (i), (ii) and (iii), or (v) the product of reaction of a bis-primary amine or a bis-secondary amine with (i), (ii), (iii) or (iv), with a polyamine which is a bis-primary, mono- or di-secondary polyalkylene-polyamine, up to 50 mol % of this polyamine optionally being replaced by a bis-primary amine or a bis-secondary amine, with the proviso that the maximum percentage is 20 mol % when the amine is hexamethylene diamine, the polymer being crosslinked by an epihalohydrin, diepoxide, dianhydride or bis-unsaturated compound, the crosslinking agent being used in an amount from 0.025 to 0.35 mol per amine group of the polyamino-polyamide, or (II) a crosslinked polymer as defined under (I) which has been alkylated (as hereinbefore defined) by an epoxide, ethylenically unsaturated compound, chloroacetic acid, propanesultone or butane sultone, the crosslinked polymer in the composition possessing the following characteristics:
(i) it does not possess any alkylating groups and is chemically stable,
(ii) it is completely soluble in water at a concentration of 10% by weight, without gel formation, and (iii) the apparent viscosity at a shear rate of 26.3 $secs^{-1}$ of a 10% by weight solution of it in water at 25°C. is at least 3 centipoises.

2. A method according to claim 1, in which the acid compound is adipic or terephthalic acid or an ester thereof, or the product of reaction of ethylene-diamine and acrylic, methacrylic or itaconic acid or ester thereof.

3. A method according to claim 1 or 2 in which the polyalkylene-polyamine is diethylene-triamine, dipropylene-triamine or triethylene-tetramine or a mixture thereof with ethylene diamine, hexamethylenediamine or piperazine.

4. A method according to any one of claims 1 to 3, in which the crosslinking agent is divinyl-sulphone, methylene-bis-acrylamide, diglycidyl ether or N,N'-bis-epoxy-propyl-piperazine.

5. A method according to any one of claims 1 to 3 in which the crosslinking agent is epichlorohydrin.

6. A method according to any one of the preceding claims in which the crosslinking agent is used in an amount from 0.025 to 0.2 mol per amine group of the polyamino-polyamide.

7. A method according to claim 6, in which the crosslinking agent is used in an amount from 0.025 to 0.1 mol per amine group of the polyamino-polyamide.

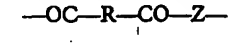
8. A method according to any one of the preceding claims in which a 10% by weight solution of the crosslinked polymer in water, at 25°C, possesses a viscosity of not more than 200 centipoises.

9. A method according to claim 8, in which a 10% by weight solution of the crosslinked polymer in water, at 25°C, possesses a viscosity of 20 to 50 centipoises.

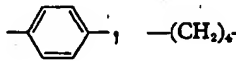
10. A method according to any one of the preceding claims in which the bis-primary amine is ethylene-diamine or hexamethylene-diamine.

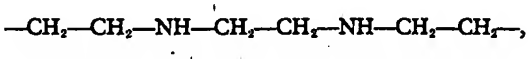
11. A method according to any one of claims 1 to 9 in which the bis-secondary amine is piperazine.

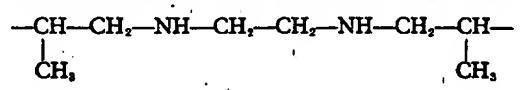
12. A method according to any one of the preceding claims in which the polyamino-polyamide consists essentially of recurring units of the formula:



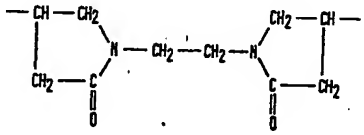
wherein R represents:



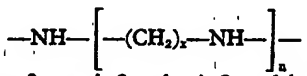




or



and Z represents:
in an amount of 50 to 100 mol %, the radical of the formula:



(II)

wherein x is 2 and n is 2 or 3 or x is 3 and n is 2; and in an amount of 0 to 50 mol %, the radical of the formula (II) in which x is 2 and n is 1 or

or in an amount of 0 to 20 mol %, the radical of the formula:
or

13. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of adipic acid and diethylenetriamine.

14. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of adipic acid and a mixture of diethylene-triamine and piperazine.

15. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of adipic acid and triethylene-tetramine.

16. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of the product of reaction of methyl itaconate and ethylene-diamine, with diethylene-triamine.

17. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of the product of reaction of methyl acrylate and ethylene-diamine, with diethylene-triamine.

18. A method according to any one of claims 1 to 12 in which the polyamino-polyamide is a polycondensation product of the reaction of methyl methacrylate and ethylene-diamine, with diethylene-triamine.

19. A method according to any one of the preceding claims in which the cross-linked polymer has been alkylated with an epoxide.

20. A method according to claim 19 in which the epoxide is glycidol, ethylene oxide or propylene oxide.

21. A method according to any one of claims 1 to 18 in which the cross-linked polymer has been alkylated by an ethylenically unsaturated compound.

22. A method according to any one of the preceding claims in which the composition contains a non-ionic, anionic, cationic, amphoteric or zwitter-ionic surface-active agent.

23. A method according to any one of the preceding claims in which the composition contains a hair strengthening agent.

24. A method according to any one of the preceding claims in which the composition is in the form of a solution, a dispersion, a gel, a cream or an aerosol.

25. A method according to any one of the preceding claims in which the composition has a pH from 2 to 11.

26. A method according to claim 25 in which the composition has a pH of from 3 to 8.

27. A method according to any one of the preceding claims in which the cross-linked polymer is present in the composition in an amount from 0.1 to 5% by weight.

28. A method according to claim 27 in which the cross-linked polymer is present in the composition in an amount from 0.3 to 1.3% by weight.

29. A method according to any one of the preceding claims in which the composition contains a water-soluble electrolyte.

30. A method according to claim 29 in which the electrolyte is sodium, potassium, calcium or ammonium chloride or acetate.

31. A method according to claim 29 or 30 in which the electrolyte is present in an amount from 0.01 to 5% by weight.

32. A method according to any one of claims 29 to 31 in which the weight ratio of electrolyte to polymer in the composition is from 0.1:1 to 1.5:1.

33. A method according to claim 1 substantially as hereinbefore described.

34. A method according to claim 1 substantially as described in any one of Examples A1 to A39.

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